

# **Testing and Refinement of Long Pathlength Liquid Core Waveguide Sensors for Autonomous *In-Situ* Analysis of the Upper Ocean**

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## **LONG-TERM GOALS**

Our research is directed toward the development of optoelectronic devices for measurement of key variables that influence oceanic biogeochemistry. The devices will have extraordinary sensitivity and versatility and, in time, their simplicity should lead to inexpensive deployments and utilization for comprehensive ocean-monitoring on long temporal scales and vast spatial scales.

## **OBJECTIVES**

The broad objectives of this work are the deployment, testing and refinement of miniature, long-pathlength spectral analysis systems for monitoring elemental distributions in seawater. The analytes of special interest in this work are iron, copper, nitrate, ammonia, nitrite and CO<sub>2</sub>-system variables (total inorganic carbon, total alkalinity, CO<sub>2</sub> partial pressure, and pH). The instrumentation under development is being designed to measure these variables with a resolution of approximately one part in a thousand. Thereby, we are developing systems capable of measurements over a wide dynamic range for each target analyte. Our in-situ devices are being developed to function autonomously in the upper ocean (0-2000m) for rapid short-term observations of chemical distributions (e.g. profiling platforms) and also observations of temporal changes on long time scales.

## **APPROACH**

Our ONR funded research has been specifically directed to the field testing of our current Spectral Elemental Analysis System (SEAS-I) and development of a refined sensor (SEAS-III) with improved sensitivity and expanded capabilities. Observations of SEAS-I performance at sea and in the laboratory have been used to improve sensor performance with respect to (a) system optics (lamp and detector stability), (b) system fluidics (reagent mixing and storage), (c) catalysts of chemical reactions and (d) development of multiple-analyte analysis capabilities.

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Key personnel: RH Byrne (Lead Scientist), EA Kaltenbacher (Lead Engineer), ET Steimle (Chemist) Xuewu Liu (Post Doctoral Research Associate), Renate Bernstein (Chemist) and Center for Ocean Technology Engineers and Technicians.

## WORK COMPLETED

During the past year SEAS-I (Figure 1) has been extensively tested in the laboratory and at sea. Tests in the laboratory demonstrated the existence of corrosion problems that interfered with iron analyses. These problems, which originated in the SEAS fluidics system, have been corrected and SEAS-I has now been shown to be capable of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  analysis at the nanomolar concentration level. Laboratory tests of SEAS-I configured for pH analyses demonstrated excellent agreement with analyses obtained on conventional spectrometers (i.e. agreement within approximately  $\pm 0.006$  pH units). However, long-term drift in the spectral content of our source lamp necessitated frequent reference measurements whereby the sample acquisition rate was compromised. The substantial efforts dedicated to solving this problem led to the identification of a lamp with suitable intensity, stability and power requirements. As such, SEAS-I is now capable of providing continuous pH measurements of very high quality. At-sea pH and  $\text{NO}_2^-$  measurements with SEAS-I identified occasional problems with the integrity of the pressure housing. The source of these problems has been identified and a protocol for eliminating future problems has been effected.



***Figure 1: SEAS-I  
[The SEAS-I sensor.]***

Work with SEAS-I has indicated that this instrument is highly effective for a variety of types of measurements. However, the inability of SEAS-I to mix a combination of reagents in sequence is analytically limiting, and the performance of commercially available miniature spectrometers does not meet our requirements. For these reasons an advanced system (SEAS-III) has been designed and is under construction. This system will be capable of multiple types of measurements with superior performance (stability and sensitivity).

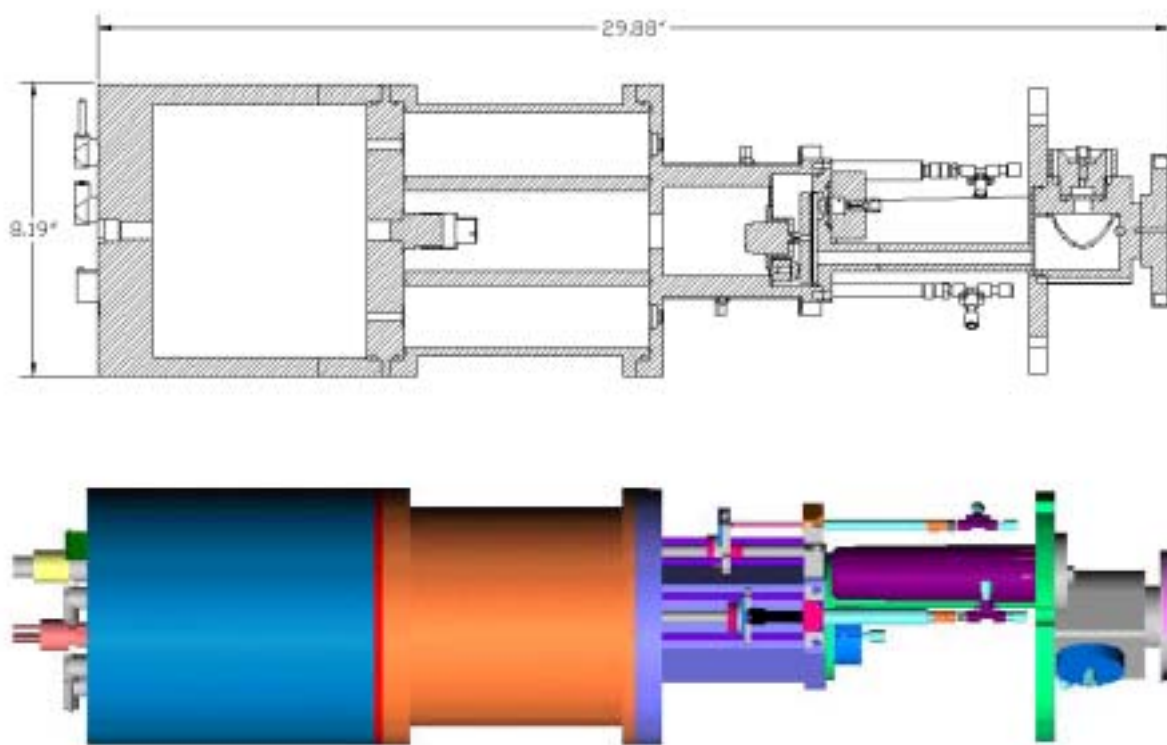
In addition to our improvements in SEAS(I+III) hardware and software, ongoing methods-development in the laboratory has led to (1) a novel spectrofluorometric system for very sensitive

ammonia analyses and (2) a novel system for CO<sub>2</sub>-system measurements wherein all primary CO<sub>2</sub>-system variables can be measured in-situ.

## RESULTS

The results of our SEAS-I investigations of NO<sub>2</sub><sup>-</sup> profiles in the Gulf of Mexico have been submitted for publication in Marine Chemistry (Steimle et al, 2001). The results of our methods developed for CO<sub>2</sub>-system parameter measurements has been accepted for publication in Analytica Chimica Acta (Byrne et al, 2001). A manuscript describing our novel spectrofluorometric system for ammonia analysis is in preparation.

The design of SEAS-III (Figure 2) is nearly complete and construction is in progress. SEAS-III incorporates a novel, multi-spectral spectrometer design (patent application submitted to USF) that should provide spectral measurements of extraordinary sensitivity and reproducibility.



**Figure 2: SEAS-III**  
*[Top view shows a cross-sectional view of SEAS-III and a solid-model of SEAS-III is shown on the bottom.]*

## **IMPACT/APPLICATIONS**

The SEAS instruments described in this work can be used to markedly extend the detection capabilities of many existing solution-based measurements obtained via absorbance spectroscopy. Applications of these sensors will include both seawater, freshwater (rivers, lakes, subterranean waters), drinking water (Yao and Byrne, 1999) and rainwater. Our instruments are simple, portable, far less expensive than conventional spectrophotometers and yet are orders of magnitude more sensitive.

## **TRANSITIONS**

The SEAS instrument tested in this project was used as a teaching aid during the USF Oceanography Camp Especially for Girls. The goal of this camp is to introduce middle-school-age girls to the world of science. Interest has also been expressed in commercial licensing of the technology developed under ONR support.

## **RELATED PROJECTS**

Our SEAS-I instrument will be the principal sensor used on a moored platform for long-term, autonomous measurements of dissolved iron ( $\text{Fe}^{\text{III}}$  and  $\text{Fe}^{\text{II}}$ ) in rainwater. The compact size, low-power requirements, small sample volume, and high sensitivity of SEAS-I make it particularly well suited for this application. This Fe measurement project is funded by the National Science Foundation (award number 9906614). The SEAS-Fe system used in this project is essentially identical to the system developed under ONR support. The principal engineering task in this work involved interfacing SEAS with a WHOI rain collector. The SEAS-I instrument will also form the basis for a project approved for funding by the Cooperative Institute for Coastal and Estuarine Environmental Technology (NOAA). This proposal will involve the use of SEAS-I to monitor Cu distributions in riverine and estuarine mixing zones.

## **REFERENCES**

J. Stone, "Optical Transmission Loss in Liquid-core Hollow Fibers", IEEE Journal Quantum Electronics, QE-8, 1972, pp. 386-8.

J. Stone, "Optical Transmission Loss in Liquid-core Quartz Fibers", App. Phys. Lett., 20, 1972, pp. 239-40.

Yao, W. and Byrne, R.H., "Determination of trace Chromium (VI) and molybdenum (VI) in natural and bottled mineral waters using long pathlength absorbance spectroscopy (LPAS). Talanta 48:277-282, 1999.

## **PUBLICATIONS**

Steimle, E.T, Kaltenbacher, E.A., and R.H. Byrne, "In-Situ Nitrite Measurements Using A Compact Spectrophotometric Analysis System", Marine Chemistry (submitted).

Byrne, R.H., Liu, X., Kaltenbacher, E., and Sell, K. (2001). "Spectrophotometric Measurement of Total Inorganic Carbon In Aqueous Solutions Using a Liquid Core Waveguide", *Analytica Chimica Acta*, (in-press).

Kaltenbacher, E.A., Byrne, R.H. and Steimle, E.T., "Design And Applications of a Chemical Sensor Compatible With Autonomous Ocean Sampling Networks", *Journal of Oceanic Engineering* (in press).

Kaltenbacher, E., Steimle, E.T. and R.H. Byrne (2000), "A compact, In-Situ, Spectrophotometric Sensor for Aqueous Environments: Design and Applications.", *Proceedings of Underwater Technology*, pages 41-45, May 23-26 Tokyo, Japan.

Byrne, R.H., Yao, W., Kaltenbacher, E. and Waterbury, R.D. (2000) , "Construction of a compact spectrofluorometer/spectrophotometer system using a flexible liquid core waveguide," *Talanta*, 50:1307-1312.

Byrne, R.H., Kaltenbacher, E. and Waterbury, R. (1999), "Autonomous *In-Situ* Analysis of the Upper Ocean: Construction of a Compact, Long Pathlength Absorbance Spectrometer Aimed at Order-of-Magnitude Improvements in the Sensitivity of Spectrophotometric Analysis," *Sea Technology*, 40(2):71-75.

Yao, W. and Byrne, R.H. (1999), "Determination of trace chromium (VI) and molybdenum (VI) in natural and bottled mineral waters using long pathlength absorbance spectroscopy (LPAS). *Talanta* 48:277-282.

Yao, W., Byrne, R., Waterbury, R. (1998), "Determination of Nanomolar Concentrations of Nitrite and Nitrate in Natural Waters using Long Pathlength Absorbance Spectroscopy", *Environ. Sci. Technol.* 32:2646-2649.

Waterbury, R., Yao, W., and Byrne, R. (1997), "Long Pathlength Absorbance Spectroscopy: Trace Analysis of Fe(II) using a 4.5 meter Liquid Core Waveguide", *Anal. Chim. Acta.*, 357:99-102.